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## Studies on Ion-Exchange Reaction of Metal Salts of Fatty Acids in Alkali-Halide Pellets by Means of Infrared Absorption Spectra

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Infrared spectra of monovalent metal salts of fatty acids were obtained in pellets of various kinds of alkali halides. Variations between the pellet and mull spectra were found in some selective combinations of the metal salts and alkali halides. These changes are due to ion-exchange reaction between the metal salts and alkali halides in the pellets. Factors which influence the reaction are: (1) lattice energy of the alkali halides; (2) energy of grinding mixtures of the metal salts and alkali halides; (3) amount of water contained in the samples; (4) the hydrocarbon-chain length of the metal salts. It is found that the reaction progresses mainly in the course of grinding the mixtures of the metal salts and alkali halides in an agate mortar, and partly in the course of the compression of the mixture in a die.

### INTRODUCTION

A number of studies have been made of anomalies in infrared spectra of polar molecules prepared by alkali-halide pellet technique.<sup>1~7)</sup> In a previous study<sup>8)</sup> on the infrared spectra of monovalent metal salts of fatty acids ( $C_nH_{2n+1}COOM$ ) we have found that, in some cases, the spectra of the metal salts in alkali-halide pellets are different from those of the same salts in mulls.

In the present paper, further observations of the anomalies are described together with discussions about possible causes of them. The lattice energy of alkali-halide crystals and the amount of water contained in the samples have been proved to influence the spectral changes. The effect of grinding and mixing the metal salts and alkali halides in an agate mortar as well as the effect of compression in a die have also been discussed.

### EXPERIMENTAL

#### Materials

Monovalent metal salts of fatty acids were prepared by the same method as that described in the previous paper.<sup>8)</sup> The metal salts thus obtained were ground to fine powders of 200 mesh, dried in a vacuum oven at 80°C (for silver salts) or at 120°C (for other salts) for two days, and kept in a vacuum desiccator containing phosphorus pentoxide.

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Alkali halides used were the highest-purity materials purchased from Nakarai Chemicals Ltd. Samples of sodium chloride, potassium chloride, and potassium bromide were recrystallized by Kyropoulos method<sup>9)</sup> from melts, while those of lithium chloride, sodium bromide, and potassium iodide were used as received. They were also ground to fine powders of 200 mesh, dried in the vacuum oven at 170°C for two days, and kept in the same way as in the case of the metal salts.

#### Preparation of the Pellets

In all the cases, 1 mg of the metal salts was mixed with 200 mg of the alkali halides by grinding for 5 min at 25°C in an agate mortar placed in a dry box, in which the relative humidity was kept at *ca.* 20 or 40% by flowing the dry nitrogen gas through it. The mixture thus obtained was put into a Hitachi model EPI-2 die (diameter 13 mm), and pressed at 10 ton for 10 min after a previous pumping for 5 min.

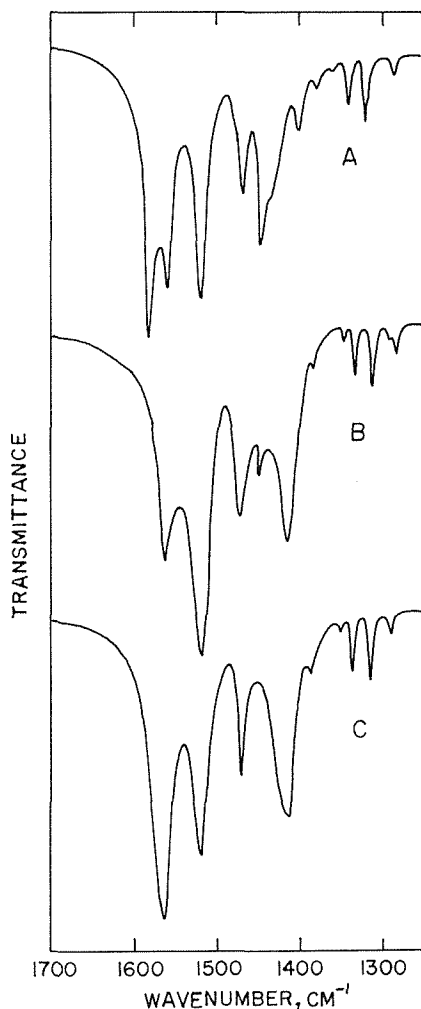


Fig. 1. Infrared spectra of silver salts of lauric acid in the lithium-chloride (A), sodium-chloride (B), and potassium-bromide pellets (C). (Relative humidity 40%).

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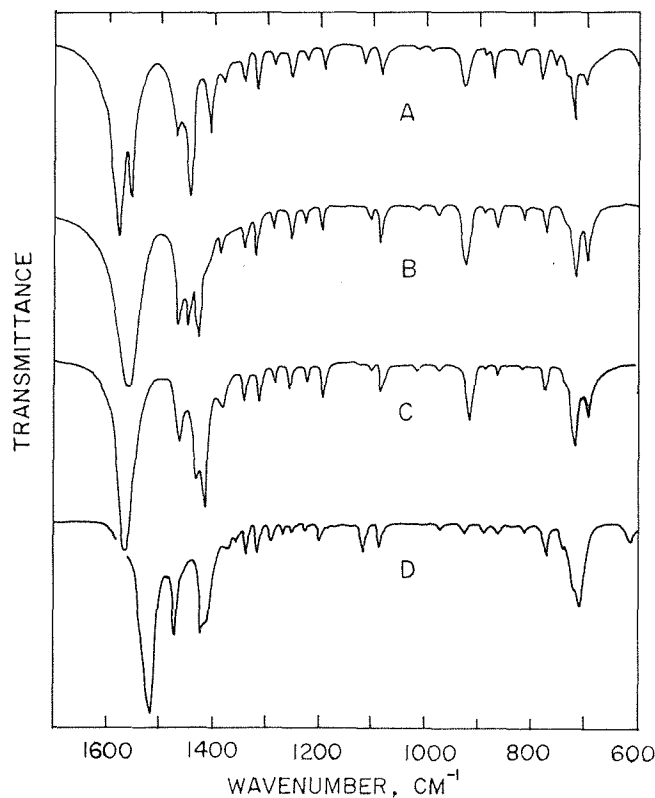


Fig. 2. Infrared spectra of lithium salt (A), sodium salt (B), potassium salt (C), and silver salt (D) of lauric acid in mulls.

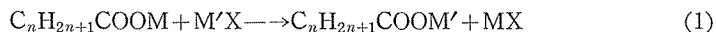
### Infrared Measurements

Infrared spectra were recorded from 4000 to 650  $\text{cm}^{-1}$  on a Hitachi model EPI-S2 spectrophotometer equipped with a rock salt prism. Spectral measurements of the metal salts in mulls were carried out using both nujol and hexachlorobutadiene.

### RESULTS AND DISCUSSION

Figures 1A, 1B, and 1C represent the infrared spectra of silver salt of lauric acid prepared by the pellet technique using lithium chloride, sodium chloride, and potassium bromide, respectively, at relative humidity of 40%. It is found from Fig. 1 that the identical sample gives rise to different spectra (A, B, and C) with common bands at 1518 and 1473  $\text{cm}^{-1}$  in the different matrices. The mull spectra of lithium, sodium, potassium, and silver salts of lauric acid are reproduced in Fig. 2, where the absorption bands due to nujol and hexachlorobutadiene are excluded. Careful comparison between Figs. 1 and 2 indicates that the lithium-chloride pellet spectrum of silver salt (Fig. 1A) is the superposition of the mull spectra of lithium salt and silver salt (Figs. 2A and 2D), the sodium-chloride pellet spectrum (Fig. 1B) is that of the mull spectra of sodium salt and silver salt (Figs. 2B and 2D), and potassium-bromide pellet spectrum (Fig. 1C) is that of the mull spectra of potassium salt and silver salt (Figs. 2C and

2D). The common bands among three spectra in Fig. 1 are due to silver salt itself.<sup>8)</sup> These facts suggest that a part of silver salt changes to lithium, sodium, and potassium salts in the lithium-chloride, sodium-chloride, and potassium-bromide pellets, respectively. In other words, the ion-exchange reaction takes place in the alkali-halide pellets as is generally shown by



where M and M' are monovalent metals and X represents a halogen atom.

The same kinds of spectral changes were also found in the various combinations of the alkali halides and monovalent metal salts of fatty acids. The results obtained are summarized semi-quantitatively in Table 1 for the metal salts of valeric and lauric acids, as examples. The numerical values in Table 1 are the ratios (in mole %) of the amounts of exchange-reaction products ( $\text{C}_n\text{H}_{2n+1}\text{COOM}'$  in (1)) to those of the original salts ( $\text{C}_n\text{H}_{2n+1}\text{COOM}$ ). They were calculated from the intensity ratio of the two bands, one is due to the  $\text{COO}^-$  antisymmetrical stretching vibration of the reaction products and the other due to the same vibration of the original salts, with reference to the calibration curves obtained from the intensity ratio of these bands in the null spectra of the mixtures (in various given proportions) of the two salts. The values might include experimental errors up to 10%. In case of the mixture of sodium salt and potassium salt, the absorption bands due to the  $\text{COO}^-$  symmetrical stretching vibrations ( $1427\text{ cm}^{-1}$  for sodium salt and  $1415\text{ cm}^{-1}$  for potassium salt) were used as the key bands instead of the bands due to the  $\text{COO}^-$  antisymmetrical stretching vibration, since the latter bands of sodium salt and potassium salt are very close to each

Table 1. Ion-Exchange Ratios (in mole %) of Metal Salts of Valeric and Lauric Acids in Various Alkali-Halide Pellets.

Metal salts	Humidity (%)	Alkali halides					
		LiCl	NaCl	NaBr	KCl	KBr	KI
$\text{C}_4\text{H}_9\text{COOLi}$	20	/	0	0	0	0	0
	40						
$\text{C}_{11}\text{H}_{23}\text{COOLi}$	20						
	40						
$\text{C}_4\text{H}_9\text{COONa}$	20	8	/	0	0	0	0
	40	32					
$\text{C}_{11}\text{H}_{23}\text{COONa}$	20	7					
	40	21					
$\text{C}_4\text{H}_9\text{COOK}$	20	9	20	20	/	0	0
	40	39	30	30			
$\text{C}_{11}\text{H}_{23}\text{COOK}$	20	8	10	10			
	40	24	20	20			
$\text{C}_4\text{H}_9\text{COOAg}$	20	16	18	21	23	35	56
	40	50	55	75	100	100	100
$\text{C}_{11}\text{H}_{23}\text{COOAg}$	20	10	11	13	13	14	17
	40	24	29	30	35	59	78

other ( $1563\text{ cm}^{-1}$  for sodium salt and  $1565\text{ cm}^{-1}$  for potassium salt). In spite of this, errors introduced to the measurements were larger than 10%, for an overlap of the  $1427\text{-}$  and  $1415\text{-cm}^{-1}$  bands was still fairly large.

It is apparent at a glance of Table 1 that the ion-exchange reaction occurs exclusively in the combinations of the alkali halides and metal salts shown in the left-bottom half of the table. For the combinations of the alkali halides and metal salts which correspond to the columns written with slant lines in Table 1, nothing can be referred to the exchange reaction, since in these cases the reaction products and the original salts are identical and no spectral change is expected even if the reaction occurs. It is also obvious from Table 1 that the amounts of the reaction products are larger in the pellets prepared at higher humidity (40%) than in those prepared at lower humidity (20%). This may indicate that water in the pellets is concerned with the dissociation of the metal salts and alkali halides to their ions as well as the mobility of the ions in the pellets.<sup>1,3,7)</sup> The amounts of the reaction products are also affected by the sorts of the alkali halides. It is seen that the ion-exchange ratios of silver salts are the largest in the potassium-halide pellets and decrease in the order of the sodium-halide and lithium-halide pellets. In Fig. 3, these ratios of silver salts of valeric and lauric acids in various alkali-halide pellets were plotted against the lattice energies of the alkali-halide crystals. This figure shows that the ion-exchange reaction is largely dependent upon the lattice energy of alkali halides as well as the humidity in the dry box as stated above. Furthermore, the effect of the hydrocarbon-chain length  $n$  of the silver salts upon the exchange reaction is shown in Fig. 4. Apparently, the ion-exchange ratio decreases with increasing the  $n$  value.

In order to discuss possible causes of the exchange reaction, the following two experiments were carried out. (1) In the combinations of the alkali halides and metal

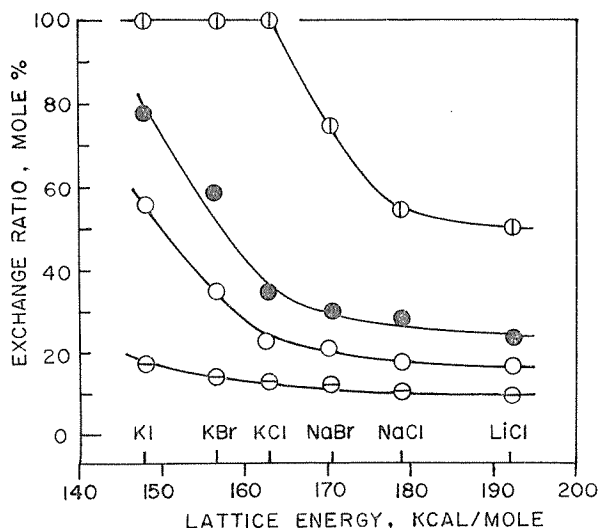


Fig. 3. Relation between ion-exchange ratio of silver salts of valeric and lauric acids in alkali-halide pellets and their lattice energy.  
 ○:  $C_4H_9COOAg$ , humidity 40%, ○:  $C_4H_9COOAg$ , humidity 20%,  
 ●:  $C_{11}H_{23}COOAg$ , humidity 40%, ○:  $C_{11}H_{23}COOAg$ , humidity 20%.

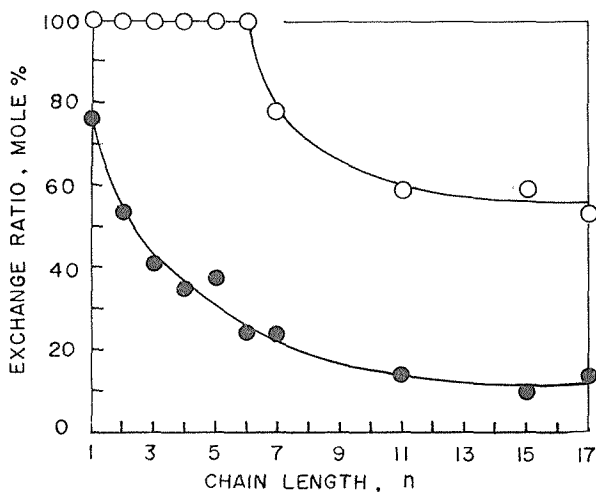


Fig. 4. Relation between ion-exchange ratio of silver salts of fatty acids in potassium-bromide pellets and carbon-chain length  $n$  of the salts. ○; humidity 40%, ●, humidity 20%.

salts, for which the exchange reaction occurs in the pellets, the alkali halides and metal salts were mixed and ground in the agate mortar under the same conditions as in the case of the pellet preparation, and their spectra were recorded in mulls. Comparison between these mull spectra and their corresponding pellet spectra shows that more than 80% of the reaction products in the pellets are obtained in this case. (2) After the alkali halides and metal salts were ground separately to fine powders, they were gently mixed by a spatula in the dry box and then pressed at 10 ton to form the pellets in the die. The infrared spectra of these pellets show smaller amounts of the reaction products (less than 30%) as compared with those (Fig. 1) of the pellets prepared by the usual method. These facts suggest that the ion-exchange reaction progresses mainly in the course of mixing and grinding the alkali halides and metal salts in the agate mortar, and partly in the course of the compression of the mixture in the die.

Keeping the pellets at 50°C for 24 hours in the vacuum oven with phosphorus pentoxide shows no further change of the spectra. This is indicative of the conclusion that the reaction does not occur after the pellets preparation is completed.

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